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The effect of thermal treatment on the structure and relaxation processes of olefinic polymers synthesized with metallocene catalysts

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Abstract

The relationships between the structure and properties have been established in several copolymers of ethylene and 1-hexene, synthesized by a metallocene catalyst. A dependency with composition and thermal history has been found. The branches cannot be incorporated into the orthorhombic crystal lattice, and consequently, structural parameters such as crystallinity and crystal lattice constants are considerably affected as 1-hexene content increases in the copolymer. The β-relaxation does not appear in the homopolymer. In the copolymers, it is shifted to lower temperature and its intensity is increased as 1-hexene content raises. On the other hand, the α-mechanism associated to motion within the crystalline regions is also moved to lower temperatures but its intensity is diminished as 1-hexene content increases in the copolymer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Metallocene catalysts; Ethylene–1-hexene copolymers; Crystallinity

1. Introduction

The use of metallocene catalysts has allowed very rapid development in the field of polyolefins. These catalysts present single-site characteristics (and very high activities) and thus all the sites produce nearly the same chain architecture [1] leading to polymers with narrow molecular weight distributions. In the case of copolymers with α-olefins, the side branches are randomly distributed in the polymer backbone.

These characteristics are very convenient for the study of the structure–property relationships since there is no need to fractionate the samples; the homogeneous distribution of comonomer is a great advantage when studying the property dependencies with the composition.

Under dynamic small strain studies, polyethylene displays at least three mechanical relaxations, designated as α, β and γ in order of decreasing temperatures, in addition to the melting point [2]. The γ-relaxation, displayed by bulk-crystallized linear and branched polyethylene and solution-grown polyethylene single-crystal mats, is found in the temperature range of −150 to −110°C. The β-relaxation, distinctly displayed only by bulk-crystallized branched polyethylene, is in the temperature range of −30 to +10°C. The α-relaxation, shown by bulk-crystallized linear and branched polyethylene and solution-grown polyethylene single-crystal mats, is in the temperature range of 30–120°C [2–4]. As expected, all peak positions increase with frequency, and each might be influenced by thermal history.

The aim of this paper is to study the effect of thermal treatment (rapid quenching or slowly cooling from the melt) on the structure and relaxation processes of several copolymers or ethylene and 1-hexene, synthesized with a metallocene catalyst.

2. Experimental

The four different ethylene–1-hexene copolymers (CEH) and the corresponding homopolymer (PE) analyzed in the current paper have been supplied by Repsol S.A. Table 1 shows the composition in 1-hexene determined by means of ^{13}C-NMR spectroscopy as well as other characteristics of the samples. Sheet specimens were obtained as films by compression molding in a Collin press between hot plates (150°C) at a pressure of 1.5 MPa for 15 min.

Each of the CEH samples was crystallized under two different conditions: Q and S. The first treatment, Q, consisted of fast cooling between plates cooled with water after melting in the press. The S specimens were slowly

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Table 1
1-Hexene composition and sample characteristics of CEH copolymers

Sample	1-Hexene (%)	Density (g cm^{-3})	M_w	M_w/M_n
PE	0.00	0.9499	202 400	2.16
CEH1	0.54	0.9369	119 100	2.25
CEH2	1.11	0.9337	116 000	2.02
CEH3	1.24	0.9290	92 600	2.24
CEH4	1.98	0.9206	11 3000	2.02

cooled from the melt, allowing the press to cool down after switching off the power. The corresponding cooling rates were, approximately, 100°C min^{-1} for the Q samples and 2°C min^{-1} for the S ones.

Wide-angle X-ray diffraction patterns were recorded in the reflection mode at room temperature by using a Philips diffractometer with a Geiger counter connected to a computer. Ni-filtered CuK$_\alpha$ radiation was used. The diffraction scans were collected over a period of 20 min between 2θ values from 3 to 43°, using a sampling rate of 1 Hz. The goniometer was calibrated with a standard of silicon.

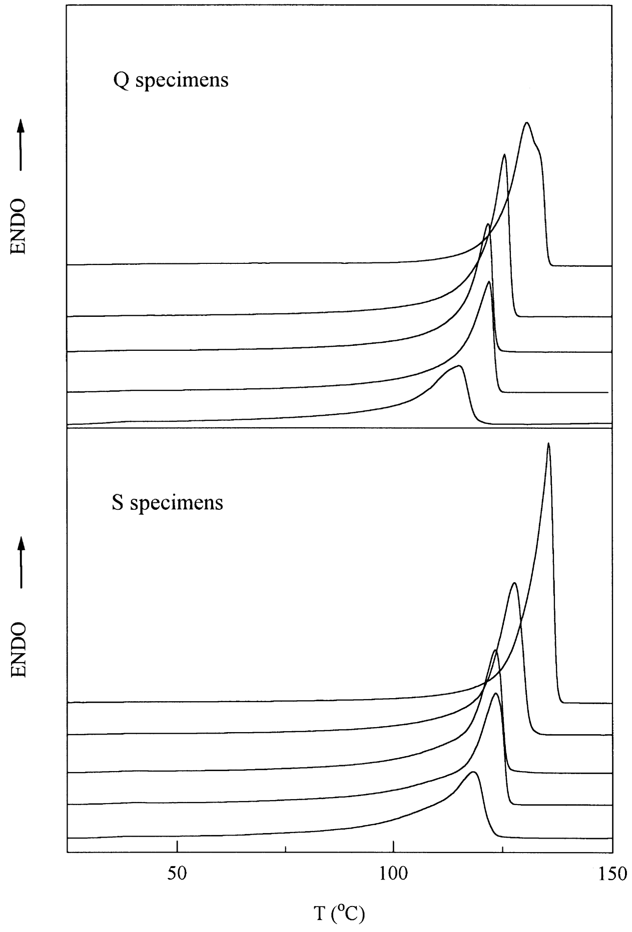

Fig. 1. DSC curves corresponding to the four CEH copolymers and the homopolymer. Top: quenched specimens (PEQ, CEH1Q, CEH2Q, CEH3Q and CEH4Q, from top to bottom) and bottom: slowly cooled ones (PES, CEH1S, CEH2S, CEH3S and CEH4S, from top to bottom).

The crystalline diffractions and the amorphous component have been separated with a fitting program that allows estimating the crystallinity of the samples. The baseline has been taken just as a straight line in the 2θ range from 8 to 36°, and no further correction has been applied. The different diffraction peaks were fitted to Voigt functions. The amorphous peak of the different samples was found to be centered at about $2\theta = 20°$. The error in the crystallinity determinations, when these are expressed as percentage, is estimated to be ±5 units.

Calorimetric analyses were carried out in a Perkin–Elmer DSC7 calorimeter, connected to a cooling system and calibrated with different standards. The sample weights ranged from 5 to 7.5 mg. A temperature range from −40 to 150°C has been studied and the used heating rate was 10°C min^{-1}. For crystallinity determinations, a value of 290 J g^{-1} [5] has been taken as the enthalpy of fusion of a perfectly crystalline material.

Viscoelastic properties were measured with a Polymer Laboratories MK II dynamic mechanical thermal analyzer working in a tensile mode. The complex modulus and the loss tangent (tan δ) of each sample were determined at 1, 3, 10 and 30 Hz over a temperature range from −150 to 150°C, at a heating rate of 2°C min^{-1}. The apparent activation energy values were calculated on loss moduli according to an Arrhenius-type equation, employing an accuracy of 0.5°C in the temperature assignment of tan δ maxima.

3. Results and discussion

3.1. Structure and thermal properties

Fig. 1 shows the DSC traces for the two thermal treatments, Q and S, in the four CEH copolymers. It is observed on the top for the Q specimens that the melting temperature (T_m), as expected, is shifted to lower temperature as 1-hexene content in the copolymer increases (there is not an appreciable T_m difference between CEH2 and CEH3 since these two copolymers exhibit quite a similar comonomer content). In addition, the melting enthalpy is reduced as 1-hexene content is raised in the copolymer. The introduction of more comonomeric units hinders the chain regularity necessary for crystallization process to take place. Consequently, crystallinity is expected to be lowered as the content in 1-hexene increases as shown in Table 2. A significant decrease in the degree of crystallinity has been observed in copolymers of ethylene-1-octene [6,7] with increasing comonomer molar fraction.

Similar features have been found for specimens slowly cooled from the melt: a shift to lower temperatures of T_m, and a depression of either melting enthalpy or crystallinity as the content of 1-hexene is raised in the copolymer. A higher value in all the different calorimetric parameters has been found in the case of S specimens, as listed in Table 2. This result could be understood by taking into

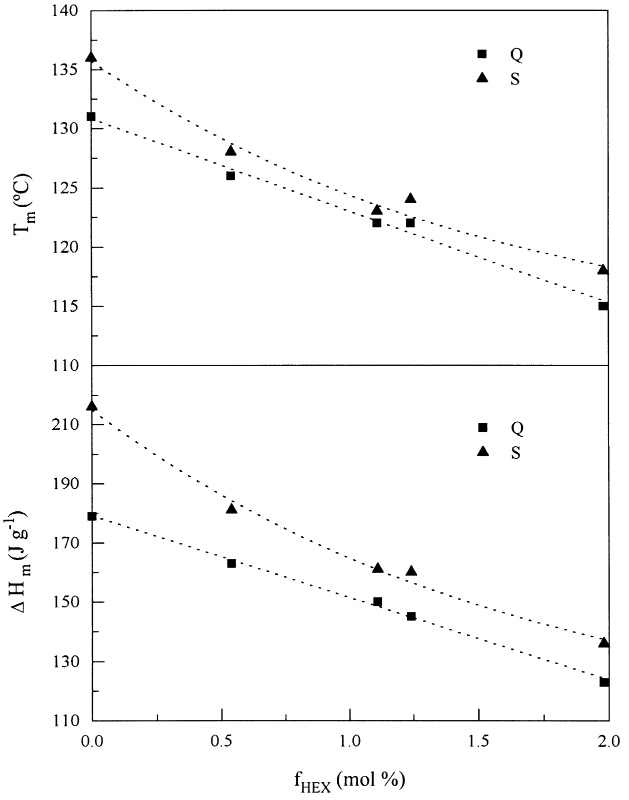

Fig. 2. Variation of melting temperature and enthalpy with composition for both thermal treatments.

account the thermal treatment procedure. Crystallization of polymers takes place at conditions far from the equilibrium, leading to the existence of a significant amorphous zone. For Q samples (the most rapidly crystallized specimens) the fast cooling limits the development of crystallites. Slow cooling (S samples) is more amenable to crystallite perfection. Therefore, it is understandable for slowly cooled copolymers to exhibit higher crystallinity (see Table 2), larger [8,9], as discussed below, and more perfect crystallites than those in quenched specimens. Moreover, T_m is shifted to higher temperatures and melting enthalpy is increased in the case of slowly cooled samples, as presented in Fig. 2.

Table 2
Melting temperatures (T_m), enthalpies of melting (ΔH) and crystallinities estimated from either DSC or X ray data of the different CEH copolymers and the corresponding homopolymer for the two thermal treatments (estimated errors: temperatures ±1°C; entalphies ±4 J g^{-1})

Sample	f_{HEX}	T_m (°C)	ΔH_m (J g^{-1})	f_c^{DSC}	f_c^{WAXD}
PES	0.00	136	216	75	75
CEH1S	0.54	128	181	62	67
CEH2S	1.11	123	161	56	65
CEH3S	1.24	124	160	55	64
CEH4S	1.98	118	136	47	58
PEQ	0.00	131	179	62	63
CEH1Q	0.54	126	163	56	61
CEH2Q	1.11	122	150	52	55
CEH3Q	1.24	122	145	50	56
CEH4Q	1.98	115	123	42	53

Polyethylene, under usual conditions, crystallizes in the typical orthorhombic lattice [10]. It is evident that the introduction of the comonomer does not influence the type of crystal formed, as depicted in Fig. 3. Some studies have shown that, in general, the alkyl branches cannot enter into the polyethylene crystal lattice and only the methyl branches are included in the lattice at a substantial degree [11–14]. The excluded branches form an interfacial region that is more ordered than the amorphous one. As comonomer content increases, the average number of consecutive ethylene units decreases and the crystallizable part becomes smaller. Consequently, crystallinity decreases (see Table 2 and Fig. 4) and the amorphous and interfacial content increase as the comonomer content raises in the copolymer. This feature has been already commented from calorimetric results. In addition, it is observed that crystallinity estimated from X-ray diffraction exhibits a higher value than that assessed by DSC measurements (Fig. 4). X-ray diffraction estimation usually provides higher values than DSC since the interfacial content does not contribute to the enthalpy.

Fig. 3 displays the different X-ray patterns found for the different copolymers under the two thermal treatments. A decrease of the intensity in the (110) and (200) diffractions is shown as the 1-hexene content increases. Moreover, the crystalline diffractions are moved to lower angles and broadened (mainly the (110) diffraction).

The different spacings change as a function of both comonomer composition and thermal treatment. Fig. 5 shows the variation of the different resolvable spacings as a function of the composition in 1-hexene for both thermal treatments. The spacings increase as the comonomer content does. This feature points out the distortion of the crystalline lattice with the increase of 1-hexene content in the copolymer since the side branches cannot be included within the lattice. The slowly cooled specimens display lower spacings than the quenched ones because of the greater perfection of crystallites in the former S specimens. The lattice constants, determined from the spacings, show a clear dependence upon the copolymer composition and thermal treatment as depicted in Fig. 6. The *a*-axis is more dependent on composition than *b*, though both of them increase as 1-hexene content is raised. It has to be said that the *b*-axis represented in Fig. 6 is the mean value of the ones from the diffractions (110) and (020). Once these two axes are known, the density of the corresponding crystal can be determined. A value of 2.54 Å has been assumed for the *c*-axis (fiber axis). Fig. 6 shows that quenched specimens exhibit crystals that are less compact than those found in slowly cooled samples, as effect of the cooling fashion. For both thermal treatments a decrease of crystal density is found as 1-hexene content increases in the copolymer.

The intensity of the diffractions is larger in the S specimens than in Q since slowly cooled specimens exhibit more

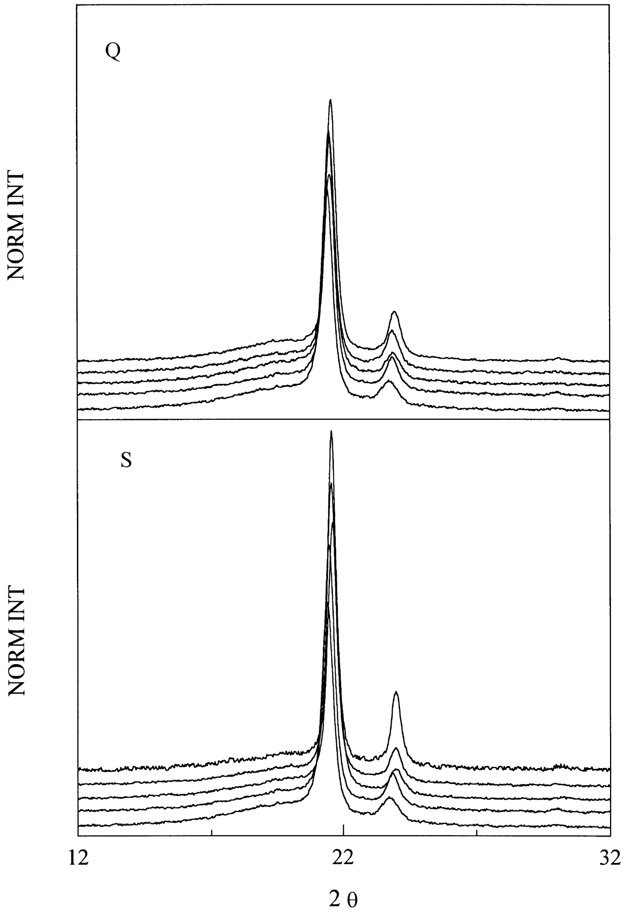

Fig. 3. X-ray diffraction patterns of the different samples for the two thermal treatments. Top: quenched specimens (PEQ, CEH1Q, CEH2Q, CEH3Q and CEH4Q, from top to bottom) and bottom: slowly cooled ones (PES, CEH1S, CEH2S, CEH3S and CEH4S, from top to bottom).

perfect crystalline regions. Consequently, the X-ray crystallinity in S specimens is higher than in quenched specimens (Fig. 4).

3.2. Viscoelastic behavior

Figs. 7 and 8 show the variation of the complex moduli and of the loss tangent for the quenched and slowly cooled specimens, respectively. The CEH3 copolymer has not been included in these two figures due to its similarity with the CEH2 results (an easier view and understanding of the different features found have been attempted with such an omission). In the upper plot of both the figures, it is observed that the storage modulus at low temperature slightly decreases as the 1-hexene content increases for both thermal treatments. This feature points out that stiffness is reduced as a consequence of the decrease in crystallinity. This modulus reduction with composition is more remarkable at higher temperature: from approximately −50°C to the end of the experiment. In this temperature range, the mechanical strength is significantly reduced with increasing comonomer content.

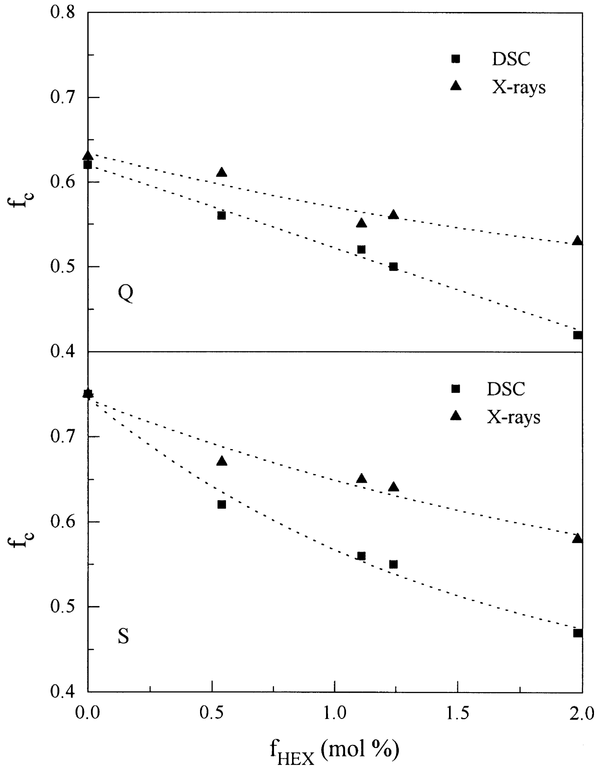

Fig. 4. Crystallinity estimated by DSC and X-ray as a function of copolymer composition for the two thermal treatments.

The better development of crystalline regions in slowly cooled specimens is responsible for the higher E values in those samples compared with the corresponding quenched copolymer.

The loss tangent plots show us a relaxation process at very low temperatures, followed by a plateau region and, finally, a continuous increase in its value, which in some particular cases becomes a maximum at high temperatures. The commented increase in tan δ value at temperatures above −50°C is dependent upon copolymer composition. Such an increase starts to occur at lower temperatures, as 1-hexene content is higher in the copolymer (Figs. 7 and 8).

In this type of copolymers, loss modulus data provide more exact information than tan δ (the relaxations (except that occurring at lowest temperatures) are less broad and the peak positions are better defined. Accordingly, data listed in Table 3, which characterize the dynamic mechanical behavior of the investigated materials (such as temperature location, intensity and apparent activation energy of the different relaxations), are taken from E'' plots. Three relaxation processes are exhibited in the four copolymers in the temperature range analyzed: γ, β and α in order of increasing temperatures. On the contrary, the homopolymer only presents two relaxation mechanisms: γ and α.

Loss moduli curves of CEH copolymers are well described as composed by contribution of different Gaussian curves, one for each observed relaxation process. Such a deconvolution does not have a theoretical basis that can

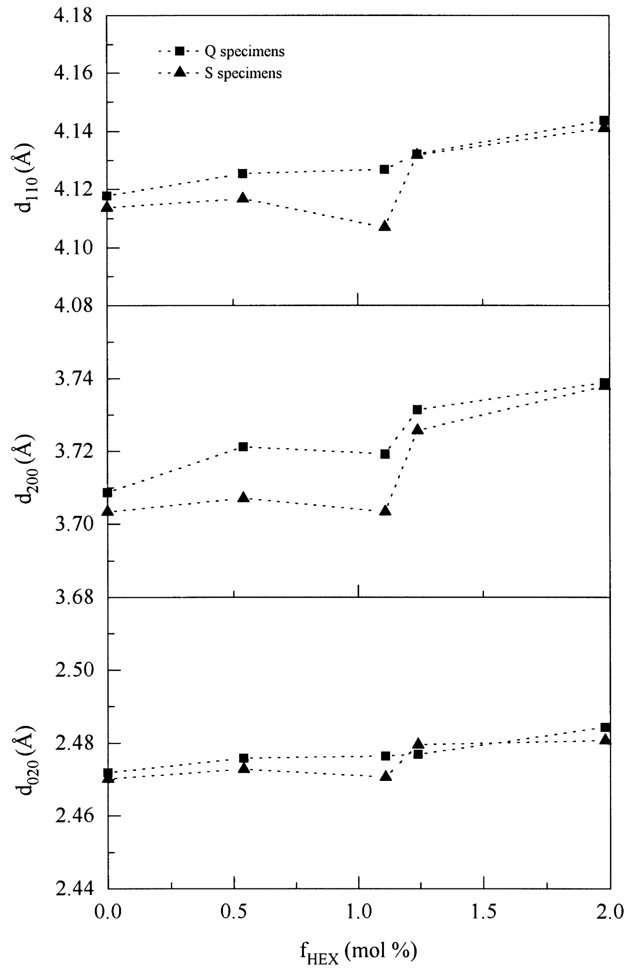

Fig. 5. Variation with composition and thermal treatment of the different diffraction spacings in PE homopolymer and the corresponding CEH copolymers.

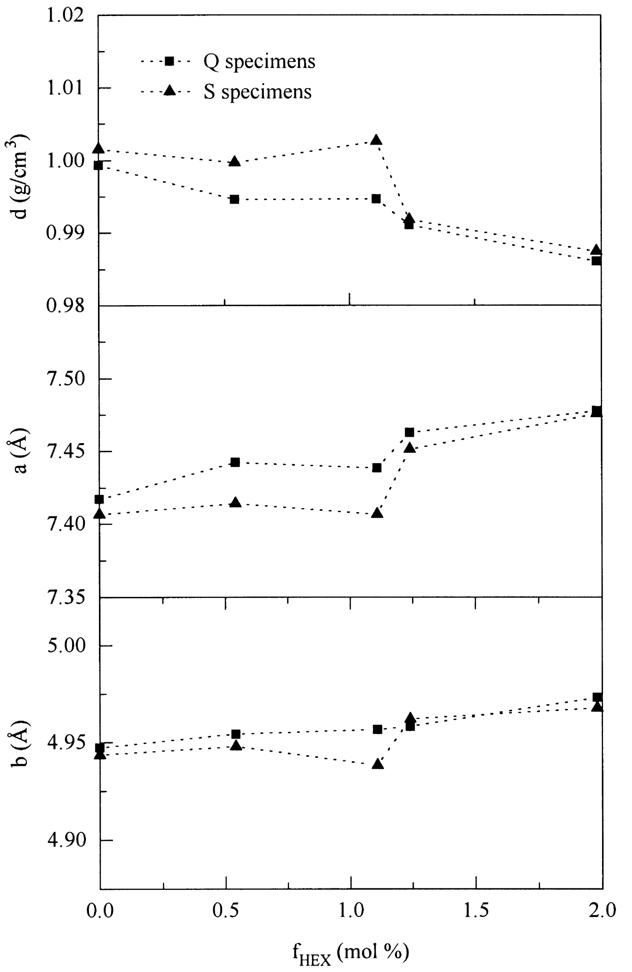

Fig. 6. Variation of the crystal lattice constants (*a* and *b*-axis and density of the crystal, *d*) as a function of copolymer composition for both thermal treatments. The *c*-axis (fiber axis) has been taken as 2.54 Å in all the cases.

explain satisfactorily the shape of the dependence of loss modulus on temperature, though some factors that can influence it are known. A method of curve deconvolution to analyze the dynamic mechanical loss curves in the region of the glass transition of several polymers has been proposed in Ref. [15] confirming the validity of this empirical approximation. In addition, it was shown that a Gaussian function provided the best fitting. In the present case, the summation of three Gaussian curves for the copolymers yields a very good overall fitting over the whole experimental range measured. This deconvolution is a very useful tool for the estimation of relative areas of the different relaxation mechanisms and for the assessment of β and α-relaxation location as the overlapping of both processes is very important. The different observed relaxation processes are analyzed separately as follows.

Table 3
Relaxation temperatures, intensities (E'' basis, at 3 Hz) and activation energies for the different relaxation processes in the homopolymer and the four CEH copolymers for the two thermal treatments

Sample	*T* (°C)			Δ*H* (kJ mol^{-1})		
	γ	β	α	γ	β	α
PES	−114.0	–	61	130	–	120
CEH1S	−116.0	−27.0	47.5	110	70	120
CEH2S	−117.5	−27.5	41.0	100	80	130
CEH3S	−118.0	−26.0	42.5	90	100	160
CEH4S	−120.0	−27.0	34.5	70	140	180
PEQ	−113.0	–	51.5	120	–	130
CEH1Q	−114.0	−28.0	39.5	120	80	130
CEH2Q	−115.5	−29.0	33.0	90	90	150
CEH3Q	−117.5	−29.0	32.5	90	100	160
CEH4Q	−119.0	−30.5	21.5	80	140	160

The γ-relaxation in polyethylene was firstly attributed to crankshaft movements of polymethylenic chains [16]. Though a lot of work concerning the γ-relaxation in polyethylene has been done, there remains no clear consensus regarding the details of the underlying motional process [17,3]. There is, however, a body of opinions that support one or more of the various models for restricted conformational transitions such as kink formation, inversion and migration [16,18–20]. This γ-process has been also found

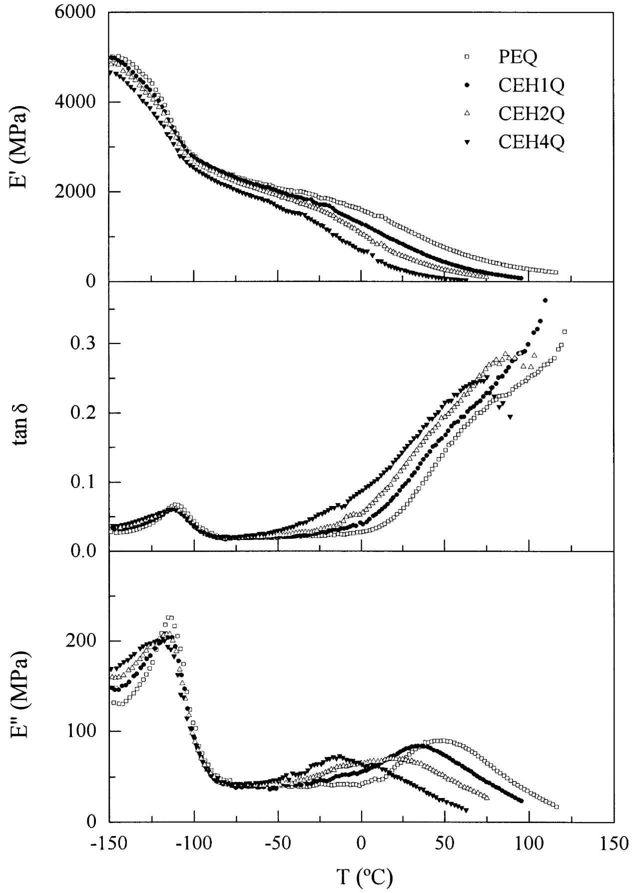

Fig. 7. Temperature dependence of the complex modulus and loss tangent of three copolymers and the homopolymer quenched from the melt.

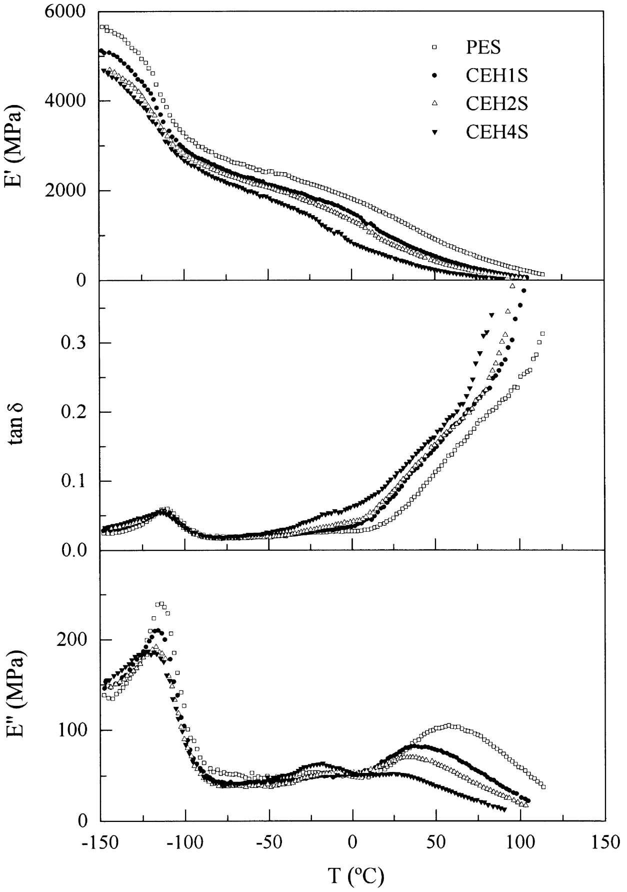

Fig. 8. Temperature dependence of the complex modulus and loss tangent of three copolymers and the homopolymer slowly cooled from the melt.

in polyesters containing oxyethylene spacers, where the oxygen atom plays an equivalent role than the methylenic groups [21–23]. This type of motion requires chains containing sequences of, at least, three or more methylenic units. Because of this requirement, the intensity of the γ-relaxation is lowered as the comonomer content is raised in the copolymer, as shown in Figs. 7 and 8. Moreover, a linear increasing relationship has been found between the relative area under the relaxation and the comonomer content, as depicted in Fig. 9. On the other hand, Fig. 10 displays that the position of the γ loss modulus peak and the calculated low activation energy are also linearly dependent upon 1-hexene molar fraction. This relaxation is shifted to lower temperatures as comonomer content increases since this process is associated with the amorphous region, which is enlarged as comonomer content is higher. A good linear relationship has been attained between its location and the content in amorphous phase in the composition range studied, as seen in Fig. 11 for both thermal treatments (a simple two phases model, amorphous and crystalline, has been assumed). The smaller crystallites developed in quenched specimens seem to impose greater restrictions to the amorphous phase than those slowly cooled. Consequently, the γ-relaxation is slightly moved to greater temperatures and the apparent activation energy is a bit higher in Q samples than in S ones, as depicted in Fig. 10 and detailed in Table 3.

The β-relaxation has been universally detected in branched polyethylenes at temperatures around −20°C but it sometimes appears, though weakly, in some samples of linear polyethylene. From the study of various polyethylenes and their copolymers, it has been concluded that this relaxation results from motions of chain units in the interfacial region [24,25]. In Figs. 7 and 8 it is observed that this relaxation process does not take place in the homopolymer PE. CEH1, for both thermal treatments, exhibits this process though very subtly. As 1-hexene content increases this relaxation becomes stronger and better defined. Its temperature location and apparent activation energy follow a linear relationship with 1-hexene content in the composition range analyzed, as seen in Fig. 9. S specimens show a weaker β-relaxation than the corresponding Q copolymer (Fig. 10). The β-process in slowly cooled samples is moved a little to higher temperatures. These features seem to indicate that the interfacial content in S specimens is lower than in Q samples and the motions within that region are slightly more restricted. On the other hand, the activation energy

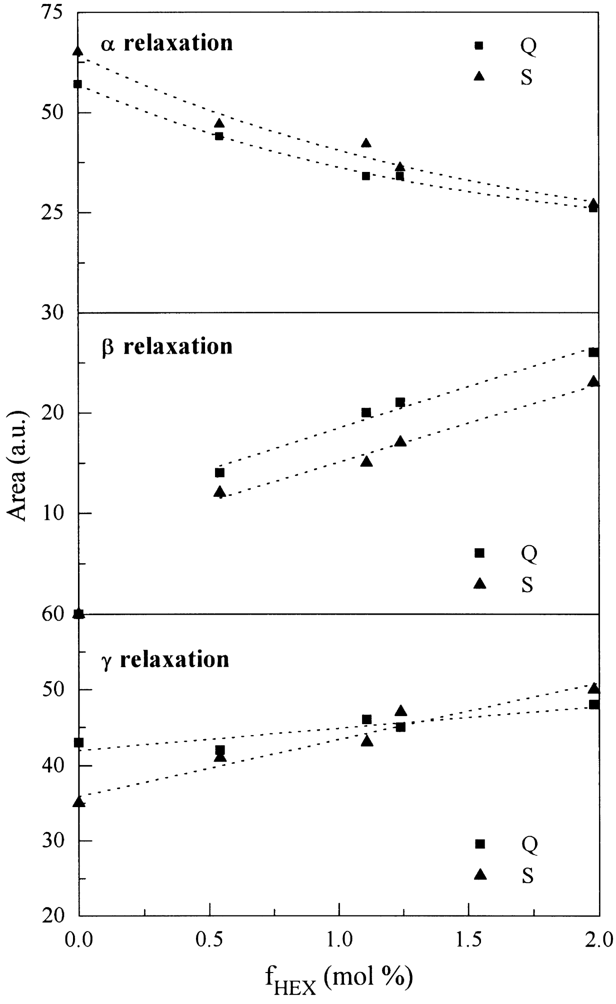

Fig. 9. Area under each relaxation process as a function of 1-hexene content in the copolymer. From top to bottom: α, β and γ-relaxation.

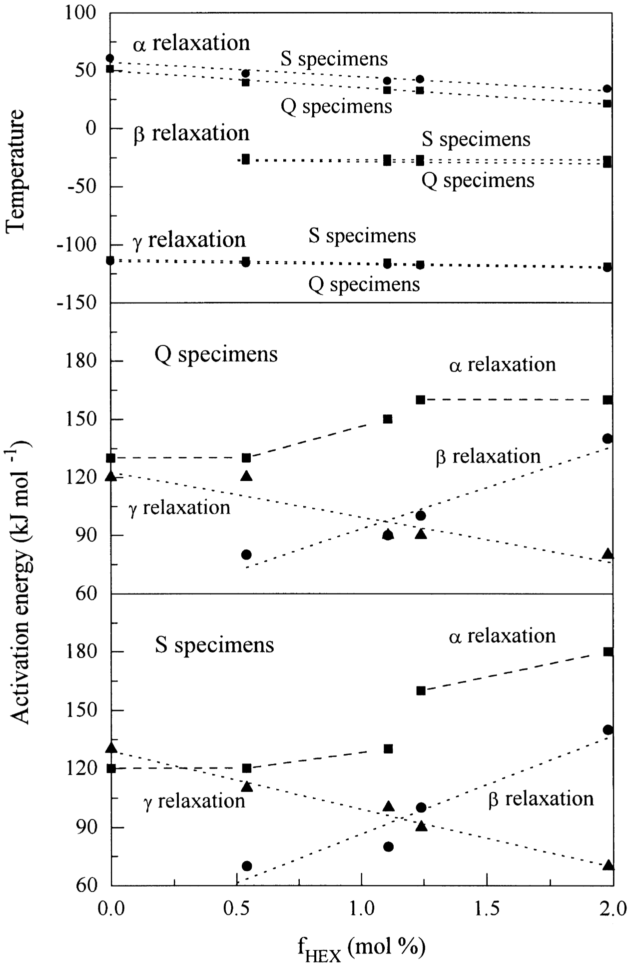

Fig. 10. Temperature location of the distinct relaxation mechanisms and the apparent activation energy values for the two thermal treatments as a function of the copolymer composition.

dependency with composition is quite similar for both thermal histories, as reported in Table 3. Its value is smaller compared to other polyethylenes and their copolymers [24,25], mainly in the case of CEH1 and CEH2. The finding of this relaxation process at the composition range analyzed (lower than 2%) is contrary to some other results of metallocenic copolymers [26], though it has to be said that in that case the comonomer unit is 1-octene. The length of the branches (or even the polymerization conditions) may have some influence on this relaxation process.

The α-relaxation in polyethylene has been associated with vibrational and reorientational motions within the crystallites [2,27]. This crystalline relaxation is recognizable in all the specimens under study (since the 1-hexene content is rather small). Quenched specimens exhibit a greater overlapping of this relaxation mechanism with the β-process, as depicted in Figs. 7 and 8, due to its lower crystalline content. A linear relationship, for both thermal histories, between temperature location and crystalline content is attained (Fig. 12) as crystallinity increases and the α-relaxation is shifted to higher temperatures. The temperature location also shows a linear relationship with the comonomer content, as seen in Fig. 10. Because of higher crystallinity and more perfect crystallites, this process occurs in S specimens at higher temperatures than in the corresponding Q samples. The apparent activation energy required for this particular motion to take place is reduced as comonomer content increases in the copolymer. It exhibits a two steps behavior which can be justified because this mechanism is formed by the superposition of two single relaxations, labeled as α and α′. The latter process does not have a very well-established origin. A translational motion of chain segments along the chain axis within the crystal lattice has been proposed in Ref. [27] as cause of this relaxation. The asymmetry of the crystalline relaxation is more significant in quenched specimens. This type of thermal treatment provides a crystallite size distribution broader than in S specimens, and this can be a reason contributing to its more obvious appearance. Fig. 10 experimentally shows that these two single mechanisms have different energetic dependency and that the difference is higher for slowly cooled specimens.

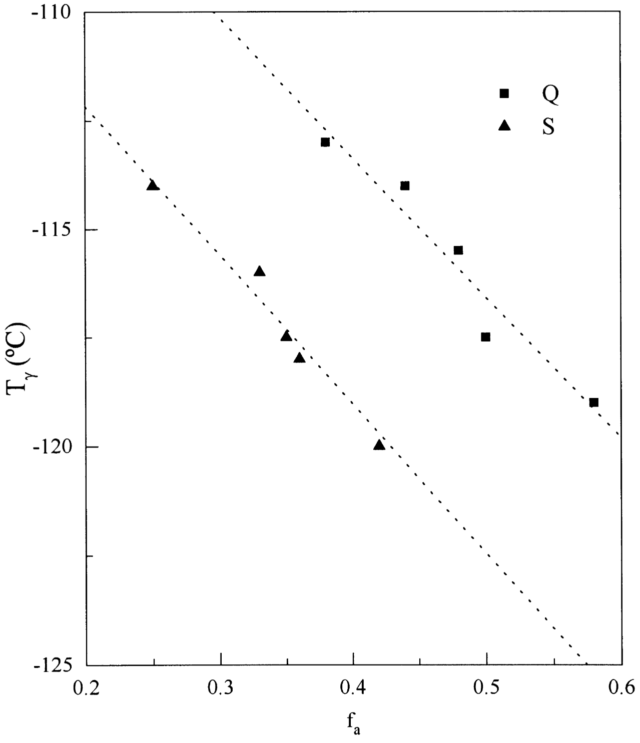

Fig. 11. The γ-relaxation location as a function of the amorphous content, determined from X-ray diffraction, for Q and S specimens.

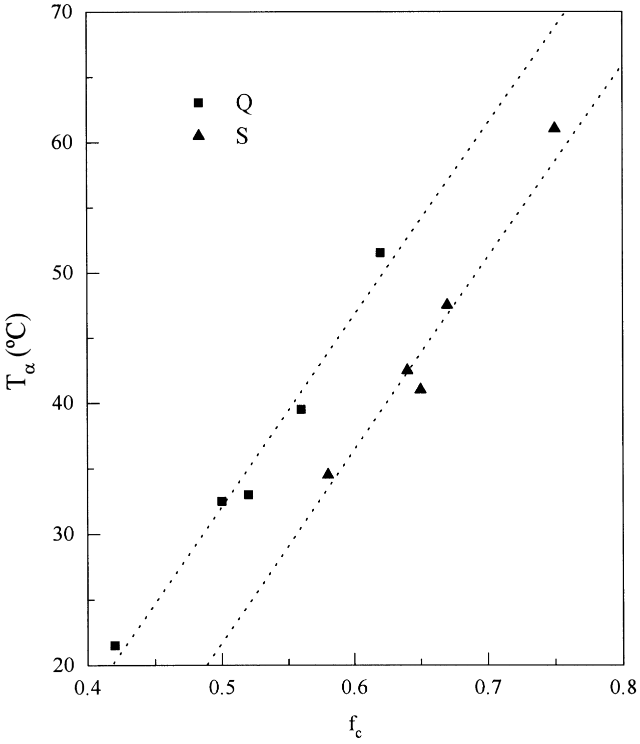

Fig. 12. The α-relaxation location as a function of crystallinity, determined from X-ray diffraction, for Q and S specimens.

4. Conclusions

The study of different properties of olefinic polymers synthesized with metallocene catalysts is a very important current issue in polymer science because of their significant practical applications. The results detailed in this paper either confirmed previous results in other polymers with a similar synthesis route or provided new details about the effect of thermal treatment on structure and relaxation processes occurring in these copolymers. Slowly cooled specimens show higher melting temperature, enthalpy and higher crystallinity than the quenched samples because of better development of the crystalline regions. The mentioned parameters are also appreciably dependent upon composition though the comonomer content is very low in the copolymers under study.

Both the variables, thermal history and composition, have very significant effects on the relaxation processes. For the γ-relaxation, which is attributed to crankshaft motion in amorphous phase, decreasing linear relationships of temperature location and apparent activation energy with copolymer composition have been found in the composition range analyzed. On the contrary, the area under this relaxation, which gives us idea of the number of groups participating in the process, increases with composition. Moreover, a linear relationship between temperature location and amorphous content, as estimated from X-ray results, has been found.

The β-mechanism is shown in the four copolymers for both thermal treatments though it does not appear in the homopolymer. The β-relaxation is shifted to lower temperatures and the intensity of the process rises as comonomer content increases. A more intense β-relaxation and a larger overlapping with the α-relaxation are observed in Q specimens. The apparent activation energy follows a linear relationship with composition for both thermal treatments.

The α-relaxation mechanism is exhibited in all the specimens analyzed. It is associated with motions in crystalline regions. Consequently, its intensity is lowered and it is moved to lower temperatures as crystallinity decreases when comonomer content increases. Since crystallinity is dependent on the thermal treatment, this relaxation occurs at higher temperatures and exhibits a higher intensity in slowly cooled specimens. A shoulder on the side of high temperatures has been experimentally observed, mainly in Q specimens. It is associated with the labeled α′ polyethylene relaxation, which is also related to the crystalline phase. These two crystalline relaxations were confirmed by the activation energy map with the composition. A linear relationship between the temperature at which the relaxation takes place and the crystallinity has been found.

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